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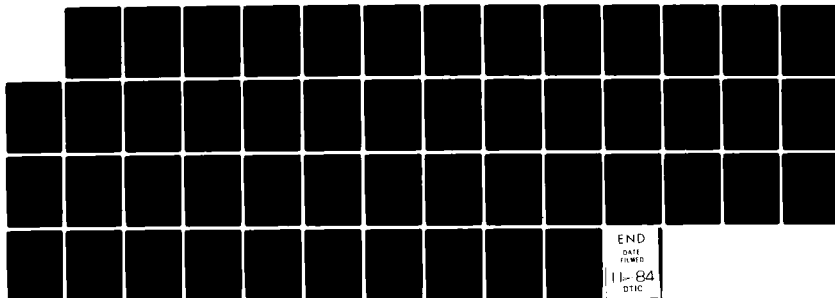
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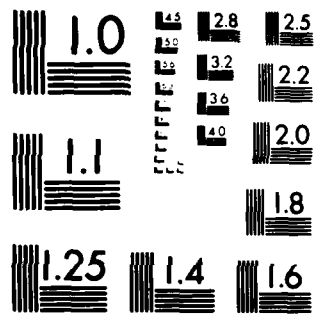
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CHARGE TRAPPING IN LOW TEMPERATURE MOS OXIDES

TECHNICAL REPORT

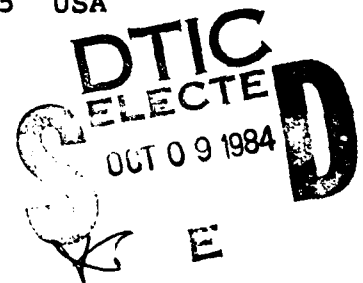
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## Charge Trapping in Low Temperature MOS Oxides

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### Abstract

Metal-oxide-silicon (MOS) capacitors were fabricated on silicon dioxide films produced at 700°C by either low pressure chemical vapor deposition (LPCVD) or high pressure thermal oxidation (HIPOX). The LPCVD process involved reaction of dichlorosilane with nitrous oxide. The HIPOX process involved dry oxygen. The LPCVD and HIPOX films were subjected to a variety of annealing treatments. We have systematically investigated the effects of these treatments by measurement of oxide charge and interface trap density before and after electron current transport across the oxide film. The as-grown electrical characteristics of HIPOX films, grown and annealed at 700°C, were comparable to those of standard dry thermal oxides grown and annealed at 1000°C. However, charge trapping in the HIPOX films was an order of magnitude larger than in the standard oxides, although well-prepared HIPOX films exhibited specific electron traps characteristic of standard dry oxides. The LPCVD oxide films required a 1000°C anneal to produce as-grown and trapped charge characteristics comparable to those of the HIPOX films. In the LPCVD oxides, a series of electron traps with cross sections ranging from  $10^{-17}$  to  $10^{-14}$  cm<sup>2</sup> were systematically altered by annealing treatments. In general, the electron traps in LPCVD oxide films produced by the nitrous oxide-dichlorosilane process were similar to those in standard wet oxides, produced by thermal oxidation in water vapor above 1000°C.

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## Table of Contents

1	Introduction	1
1.1	Summary of Research Program	2
1.2	Personnel Involved in This Program	2
2	Experimental Details	4
2.1	Sample Preparation	4
2.2	Measurement Procedures and Program	5
3	Experimental Results	8
3.1	As-Fabricated LPCVD Oxide Films	8
3.2	Avalanche Injection in LPCVD Oxides	10
3.2.1	LPCVD Oxides Fabricated at 700°C	12
3.2.2	LPCVD Oxides Annealed at 1000°C	13
3.3	Standard and HIPOX Thermal Oxide Films	14
4	Discussion and Conclusions	15
4.1	The Quality of LPCVD Oxide Films	15
4.2	Electron Injection in LPCVD Oxides	16
4.3	Properties of HIPOX Films	17
4.4	Oxide and Interface Electron Traps	17
4.5	Conclusions	20
	List of References	22
	List of Tables	
Table I.	Oxide Charge in (111) Dry Thermal Oxides	24
Table II.	Oxide Charge in (111) Deposited Oxides	25
Table III.	Oxide Charge in (100) Deposited Oxides	26
Table IV.	Oxide Charge in (111) Dry HIPOX Oxides	27
Table V.	Thermal Oxide Initial Capture Efficiency	28
Table VI.	LPCVD Oxide Initial Capture Efficiency	29
Table VII.	Dominant Electron Traps in Thermal Oxides	30
Table VIII.	Dominant Electron Traps in Deposited Oxides	31
Table IX.	Bulk and Interface Traps in HIPOX Films	32
	List of Figure Captions	33

## Charge Trapping in Low Temperature MOS Oxides

### 1 Introduction

The study of charge trapping associated with electron injection is a necessary component of dielectric materials characterization for microelectronic applications. This applies in particular to MOS oxide films used in both gate insulator and field insulator configurations. There are device instabilities associated directly with trapping of electrons injected into MOS insulators. These include inadvertent hot electron effects in short channel transistors and the effects of intentional injection in floating gate or dual dielectric memory structures during read/write operations. In addition, dielectric breakdown, which is a ubiquitous problem in VLSI microelectronics, has both long-standing and recent association with current injection.

During the second and third year of work on this contract, a charge trapping study was designed and executed. The purpose of this program was to determine the effect of specific device processing steps on the electrical properties of MOS insulator films. This research was conducted on silicon dioxide films prepared by several methods which have potential for technological development. In particular, the oxide fabrication methods studied were capable of producing VLSI-scaled insulator films (10-100 nm) in reasonable times (0.1-10 hr) at low temperatures (at and below 700°C). Low fabrication temperature is the primary requirement which VLSI scaling imposes on insulator technology [1].

## 1.1 Summary of Research Program

The oxide film processing steps investigated were the following: (A1) Low pressure chemical vapor deposition of silicon dioxide films (LPCVD) or (A2) high pressure thermal oxidation of silicon (HIPOX). (B1) Inert ambient annealing at or above the deposition temperature, for LPCVD oxide films. This is PDA, post deposition annealing. (B2) Inert ambient annealing at the oxidation temperature, for HIPOX films. This is POA, post oxidation annealing. (C1) Annealing in a hydrogen containing ambient (forming gas) at low temperatures subsequent to MOS research capacitor fabrication on LPCVD oxides. (C2) Annealing in a nitrogen ambient at low temperatures subsequent to MOS research capacitor fabrication on HIPOX films. In the present program, research capacitors were fabricated on both deposited oxide films and thermal oxide films by deposition of evaporated high purity aluminum in vacuum. The annealing step C1 or C2 is therefore PMA, post metallization annealing.

These processing steps were also investigated for conventional high temperature dry thermal oxides. In the context of the overall objectives of the present program, these oxides, with POA and PMA treatments, are standards for gate insulators. They were included in the present study specifically as a benchmark.

The electrical properties investigated were those summarized by the oxide charge classification scheme proposed by Deal [2]. These are  $Q_f$ , oxide fixed charge,  $Q_{it}$ , interface trap charge, and  $Q_{ot}$ , oxide trapped charge. Particular emphasis was placed on the development of bulk oxide trapped charge  $Q_{ot}$  as a result of electron injection and current flow in the oxide.

## 1.2 Personnel Involved in This Program

The LPCVD oxides and the conventional high temperature dry thermal oxides were produced in the Microelectronic Fabrication Facility of the Sherman Fairchild Laboratory at Lehigh University. The development of a chemical vapor deposition facility at Lehigh was supported in part by funds and personnel (Professor Butler and Dr. Vogel) from the present contract. The furnace and gas delivery system was designed as a general purpose facility, capable of producing a variety of both semiconductor (polycrystalline silicon) and insulator (glassy silicon dioxide and amorphous silicon nitride) film materials. The construction of the general facility was outside the scope of this contract,

and thus is not described in detail in this report.

The HIPOX oxides were produced as part of a broad cooperative research program with the U. S. Army ERADCOM Device Electronics and Electronic Technology Laboratories at Ft. Monmouth, New Jersey. The high pressure oxidation chamber and the HIPOX fabrication were designed, implemented, and executed by Dr. Robert Zeto and coworkers of ERADCOM DELET-ED. Mr. Leonard Trombetta, a Lehigh Ph. D. candidate executing his dissertation as a staff member at DELET-ED, was a central participant in this effort. Mr. Trombetta was not supported by this contract.

The measurements of oxide charge and oxide charge generation in capacitors prepared on the various low temperature oxides were executed by Ms. Mary Ellen Zvanut. Miss Zvanut also assumed primary responsibility for analysis and interpretation of experimental data. She was assisted in this by Dr. Stephen L. Titcomb. These activities were supported by the contract.

Overall direction of this project was the responsibility of Professor Feigl. Professor Butler was responsible for fabrication of LPCVD oxide films.



## 2 Experimental Details

### 2.1 Sample Preparation

The MOS insulator films studied included silicon dioxide produced by the surface-catalyzed reaction of a 1:10 volume ratio mixture of dichlorosilane and nitrous oxide maintained at a total pressure of approximately 1 torr [3]. The oxides were deposited on polished and cleaned 0.1-0.2 ohm-cm, p-type, (100) and (111) silicon substrates in a hot wall reaction/deposition tube. LPCVD oxides were prepared at approximately 700°C. Deposition times were 60 to 120 minutes, and the average deposition rate was (0.25±0.01) nm/min.

The resulting 10-60 nm thick deposited oxides were subjected to a variety of post-deposition annealing steps (PDA) in either dry nitrogen or dry oxygen ambients. The latter choice was dictated by previous success using an oxygen carrier gas to produce silicon dioxide films from the liquid-source organic reactant LPCVD process previously studied (see previous technical report on the TEOS LPCVD studies). The PDA procedures investigated include the following:

1. 700°C PDA in dry O<sub>2</sub> for 30 minutes.
2. 700°C PDA in dry N<sub>2</sub> for 30 minutes.
3. 800°C PDA in dry N<sub>2</sub> for 30 minutes.
4. 1000°C PDA in dry N<sub>2</sub> for 30 minutes.

The oxide surface was metallized by filament evaporation of high purity aluminum through a contact mask. This produced an array of circular dots of area 0.01-0.02 cm<sup>2</sup>. A PMA treatment at 450°C in 4/1 N<sub>2</sub>/H<sub>2</sub> for 20 minutes was performed on half of each wafer so that a set of samples both with and without PMA for each PDA treatment could be studied.

The second class of low-temperature oxide films examined in this study were the HIPOX films [4]. These oxides were produced by low temperature thermal oxidation of 6mm x 18mm, 0.1 ohm-cm,

p-type, (100) silicon substrates in nominally dry high purity oxygen gas admitted into a dead-end oxidation chamber at approximately 500 atmospheres pressure. HIPOX films were prepared at a variety of temperatures between 600 and 900 °C. A detailed study was made on oxides grown at 685 °C for 60 and 165 minutes. Some of the HIPOX films were given an in situ POA treatment in dry nitrogen at 685 °C for 300 min. Research capacitors were prepared by aluminum metallization with an electron beam evaporation system. Individual research capacitors were circular dots of area 0.003 cm<sup>2</sup>. A PMA treatment in dry nitrogen at 450 °C for 30 min was given to half of the research samples.

The third type of MOS insulator studied were conventional high temperature dry thermal oxides. These were produced by a 40 minute 1000 °C oxidation of 0.1-0.2 ohm-cm, p-type, (111) silicon substrates in nominally dry high purity oxygen gas flowing through an open-end oxidation chamber at one atmosphere pressure. Some of these oxides were given a POA treatment in dry nitrogen at 1000 °C for 30 min. A PMA treatment at 450 °C in 4/1 N<sub>2</sub>/H<sub>2</sub> for 20 minutes was performed on half of each wafer following filament evaporation of high purity aluminum capacitor dots (area 0.015 cm<sup>2</sup>).

## 2.2 Measurement Procedures and Program

The oxides studied were characterized by their charge properties before, during, and after pulsed avalanche injection of electrons. An RF injection circuit similar to the one described by E.H. Nicollian and J.R. Brews [5] was used to generate electron current pulses across the oxide. A feedback network was used to maintain the average DC current constant throughout a given avalanche injection run. Throughout the course of a given injection run, the 1 MHz C-V flatband voltage  $V_{fb}$  was automatically recorded at pre-set time intervals. The basic experimental data was  $V_{fb}$  vs.  $F$ , the cumulative electron injection fluence. The fluence  $F$  is the product  $Jt$ , where  $J$  is the DC current density flowing during avalanche injection and  $t$  is the cumulative time of injection. These data were converted to an oxide charging curve  $Q_{ot} + Q_{it}$  vs.  $F$  using the relation

$$Q_{ot} + Q_{it} = -C_{ox} \Delta V_{fb} \quad (1)$$

where  $C_{ox}$  is the device capacitance per unit area in strong accumulation and  $\Delta V_{fb}$  is the change in  $V_{fb}$ .

Conventional capacitance techniques were used to determine the charge characteristics of the oxide film before and after

avalanche injection. In particular,  $Q_f$  was determined from the position of the conventional flatband voltage obtained from depletion approximation analysis of the high frequency capacitance-voltage (hf C-V) characteristic of the as-grown device. The measured flatband voltage was compared with that for an ideal charge-free device. This method for separation of  $Q_f$  and  $Q_{it}$  is an arbitrary procedure for describing experimental results whenever  $Q_{it}$  is of the order of  $Q_f$ , or is larger than  $Q_f$ . Deal [6] and Nicollian and Brews [7] have commented in detail on this problem.

In principle,  $Q_{it}$  can be determined from the voltage stretchout of the hf C-V characteristic. In practice, interface trap charge was determined from a comparative analysis of the high frequency and low frequency C-V characteristics (high-low method). These results were summarized as the mid-gap interface trap density, defined as  $D_{it}$ . The low frequency characteristics of a capacitor were determined from the current-voltage characteristics measured in response to an adiabatic linear ramp voltage applied to the capacitor under dark conditions (i.e., no visible or ultraviolet light). This is the quasistatic dark I-V response, or the quasistatic method, developed by Kuhn [8]. The analytical method used to determine the interface trap density was the high-low comparison method developed by Castagne and Vapaille [9].  $D_{it}$  values were always determined from comparison of the measured high-low C-V characteristics with a model (ideal) device with  $D_{it} = 0$ . They are never specified as a change in mid-gap interface trap density.

A similarly arbitrary separation has been made in analyzing the electrical characteristics of MOS capacitors after avalanche injection of an electron current. In this case,  $Q_{it}$  was determined from the change of the flatband voltage of the capacitor (as determined from hf C-V) relative to the as-prepared value measured prior to the injection run.  $D_{it}$  was again determined from comparison of hf C-V and  $Q_{it}$  quasistatic characteristics, as just described.

The following sequence of oxide film characterization experiments were executed:

1. Dark current at a static bias of 1 MV/cm at room temperature.
2. 1 MHz C-V characteristic at room temperature.
3. Bias-stress at a static bias of 1 MV/cm at 200°C.
4. 1 MHz C-V characteristic at room temperature.
5. Quasi-static ramp I-V characteristic at room temperature.

6. Avalanche injection of electrons and measurement of the oxide charging curve at room temperature.

7. Repetition of steps four and five.

Typically, full execution of this sequence involved a number of capacitors on a given oxide film.

### 3 Experimental Results

#### 3.1 As-Fabricated LPCVD Oxide Films

Standard commercial equipment was used to measure room temperature dark current and the effects of bias-temperature-stress on as-prepared capacitors fabricated on LPCVD oxide films. These measurements were those listed as steps 1 through 4 of the oxide film characterization sequence described in Section 2.2. The following results were obtained:

1. As-deposited oxides less than 30 nm thick had static leakage currents in the range of 1 milliamp/cm<sup>2</sup> under 1 MV/cm bias at room temperature. This leakage current was significantly reduced in oxides greater than 30 nm thick. Thickness was measured by ellipsometer.
2. Oxides subjected to PDA at 700-800°C but not to PMA had static leakage currents of the order of, but generally less than, 0.01 microamps/cm<sup>2</sup>, and exhibited large and anomalous bias instabilities at 100-200°C. These phenomena were not present in LPCVD oxides subjected to PDA at 1000°C.
3. LPCVD oxide films subjected to PDA in either N<sub>2</sub> or O<sub>2</sub> at 700°C and to a standard PMA treatment<sup>2</sup> exhibited characteristics similar to standard 1000°C dry thermal oxide films, with the exception of anomalously high static dark currents. Thermal oxides given standard annealing treatments exhibited dark currents of order 10 picoamp/cm<sup>2</sup> or less, while the deposited oxides had dark currents in the range of 100 picoamp/cm<sup>2</sup>.

The measurements listed as steps 4 and 5 of the oxide film characterization sequence described in Section 2.2 are summarized under the two columns listed as "As-Grown Charge" in Tables II and III. These measurements were performed on capacitors not previously subjected to steps 1 and 3 of the sequence. Tables II and III refer to LPCVD oxides grown on (111) and (100) Si substrates, respectively. The results quoted are averages of data obtained from measurements on a number of capacitors

fabricated on each type of LPCVD oxide listed in the tables.

Some representative measurements on specific capacitors are shown in Figures 1-3. These three figures each contain normalized experimental high-frequency and low-frequency C-V characteristics obtained on as-fabricated capacitors (before electron injection) and on the same capacitors after electron injection. Figure 1 contains data obtained from an LPCVD oxide film, and on this figure the C-V characteristics for an ideal MOS capacitor are shown. The ideal characteristics were obtained via standard techniques summarized in Nicollian and Brews [10], assuming  $Q_f = Q_{it} = Q_{ot} = 0$ , i. e., a charge-free oxide. The calculated value of the normalized flatband capacitance for the ideal device,  $C_{fb}/C_{ox}$ , is also shown in Figure 1.  $Q_f$  was obtained from the shift of the measured high frequency C-V flatband voltage from the ideal flatband voltage.  $D_{it}$  was obtained from the high-low comparison technique, as discussed in Section 2.2.

Statistical analyses of the data averages in Tables II and III indicate the following results regarding the separate effects of silicon substrate orientation, PDA, and PMA. Note again that results summarized for  $Q_f$  are in fact representative of the net interface charge  $Q_f + Q_{it}$ , since  $Q_{it}$  was indeterminable but large (as evidenced by the measured values of  $D_{it}$ ).

1.  $Q_f$  on (100) Si was approximately one-half of  $Q_f$  on (111) Si. However, within the limits of the measurement technique, substrate orientation had no statistically significant effect on  $D_{it}$ .
2. PDA at 700°C in  $N_2$  had no statistically significant effect on either  $Q_f$  or  $D_{it}$ . PDA at 1000°C also had no effect on  $Q_f$ , but produced an order-of-magnitude decrease in  $D_{it}$ . This last result is shown in Figure 4, in which calculated values of  $D_{it}$  are displayed.
3. Standard PMA produced a factor-of-three decrease in both  $Q_f$  and  $D_{it}$ .

A comparison can be made between as-grown charge in LPCVD oxides and as-grown charge in standard high-temperature thermal oxides. Results from LPCVD oxides are in Table II and results from standard thermal oxides are in Table I. These results indicate the following:

1. LPCVD oxides subjected to 700°C PDA in either  $N_2$  or  $O_2$  and to PMA had a factor-of-three greater  $Q_f$  than the standard oxide with POA and PDA. These LPCVD oxides also had an order-of-magnitude larger  $D_{it}$  than the annealed standard oxides (see Figure 4).

2. LPCVD oxides subjected to  $1000^{\circ}\text{C}$  PDA in  $\text{N}_2$  and to PMA had a factor-of-three greater  $Q_{\text{f}}$  than the standard oxide with POA and PDA. These LPCVD oxides, however, had  $D_{\text{it}}$  less than a factor-of-two greater than  $D_{\text{it}}$  in the annealed standard oxides.

### 3.2 Avalanche Injection in LPCVD Oxides

The measurements performed in connection with electron avalanche current injection in LPCVD oxides were listed as steps 4 through 7 of the oxide film characterization sequence described in Section 2.2. High-frequency and low-frequency C-V characteristics measured on representative capacitors after electron injection are shown in Figures 1-3.  $D_{\text{it}}$  values calculated from such data are shown in Figure 5.  $Q_{\text{ot}}$  values were calculated from the shift of the experimental high-frequency flatband voltages measured before and after avalanche injection, as indicated in Figure 1.

The high-frequency flatband voltage was also tracked automatically during the course of each current injection run on each research capacitor. Oxide charging curves were determined from these data by the procedure described in Section 2.2. Representative charging curves obtained on capacitors with LPCVD oxide dielectrics are displayed in Figures 6-8.

The results of this measurement program are summarized under the three columns listed as "Post-Injection Characteristics" in Tables II and III for LPCVD oxides grown on (111) and (100) Si substrates, respectively, and in Tables VI and VIII. In all cases, the results quoted are averages of data obtained from measurements on three to five capacitors fabricated on each type of LPCVD oxide listed in the tables.

Whenever possible,  $Q_{\text{ot}}$  and  $D_{\text{it}}$  values listed in Tables II and III were determined at an injected current fluence of  $0.05 \text{ C-cm}^{-2}$  (i.e.,  $3 \times 10^{17}$  injected electrons/ $\text{cm}^2$ ). For capacitors in which the buildup of oxide trapped charge and interface traps was large and rapid, this was not possible. In these cases,  $Q_{\text{ot}}$  and  $D_{\text{it}}$  values were determined at a fluence of  $0.001 \text{ C-cm}^{-2}$  ( $6 \times 10^{15}$  injected electrons/ $\text{cm}^2$ ).

The oxide charging curves were analyzed in terms of a first order kinetic model involving the buildup of negative charge throughout the bulk of the oxide film and positive charge in the vicinity of the oxide-silicon interface. This procedure has been previously described in great detail [11, 12]. The kinetic model is summarized in the following equations:

$$(Q_{ot} + Q_{it})/e = - N_{ot} + N_{it} \quad (2)$$

$$N_{ot}(F_A) = N_{ot}(\infty)\{1 - \exp(-\sigma_c F_A)\} \quad (3)$$

$$N_{it}(F_A) = N_{it}(\infty)\{1 - \exp(-\sigma_e F_A)\} \quad (4)$$

Equation (2) defines the charging curves presented in Figures 6-8 in terms of the basic experimental quantity  $V_{fb}$  (see Equation (1) in Section 2.2). Equation (3) is interpreted in terms of a centroid-weighted areal density of electron trapping centers  $N_{ot}(\infty)$  distributed throughout the bulk of the oxide film. These trapping centers are characterized by an electron capture cross section  $\sigma_c$ . Equation (4) is interpreted in terms of the buildup of fast and slow donor-like traps in the vicinity of the oxide-silicon interface. This buildup produces the "anomalous positive charge" widely observed during electron injection into silicon dioxide films [13]. The effective cross section for this process, relative to the injected electron flux  $J/e$ , is  $\sigma_e$ , and the saturated areal density of net interface trap charge is  $N_{it}(\infty)$ .

Results of such analyses were summarized as an initial capture efficiency, which is the fraction of injected electrons trapped in the oxide film bulk in the limit  $F_A = 0$ . Initial capture efficiency was obtained as the product  $\sigma_c N_{ot}(\infty)$ , or as the slope of the oxide charging curves at  $F_A = 0$ . These results are tabulated for LPCVD oxide films in Table VI. The capture cross section  $\sigma_c$  is tabulated in Table VIII, for the LPCVD films for which it could be reliably determined.

Before summarizing the experimental results on electron injection, limitations specific to these particular samples should be noted. The thickness and quality of oxide films limit the magnitude of the voltage applied during AC avalanche injection. In particular, oxide breakdown places a maximum on the amplitude of the negative half cycle of the injecting voltage pulse, thereby limiting the size of the positive peak which provides the silicon avalanche field [14]. This problem was particularly serious in LPCVD oxide films not subjected to PDA at 1000°C.

Because of this problem, not all samples were injected at the same current density. Since the trapping characteristics of an oxide may depend on the injected current density [15], some LPCVD oxides were injected at both low and high current densities. Indeed, some variation of oxide charging curves with injected electron current density was observed. In general, as previously observed, these variations were small and were not studied in



detail [11]. Whenever possible, comparisons between different oxide films were made using injection data obtained at similar current densities. In particular, the comparison of LPCVD oxides given different annealing treatments (the  $Q_{ot}$  column of Tables II and III), were determined from injections performed at  $0.6 \mu\text{A-cm}^{-2}$ . However, the data in Figure 9, a comparison of the LPCVD, HIPOX, and thermal oxides, result from injection at  $6.0 \mu\text{A-cm}^{-2}$ .

Statistical analyses of the tabulated experimental results were performed. These were similar to those done for the as-grown LPCVD oxide characteristics. The results are summarized below.

### 3.2.1 LPCVD Oxides Fabricated at $700^\circ\text{C}$

The samples of primary interest in this study were LPCVD oxides fabricated entirely at temperatures at and below  $700^\circ\text{C}$ . Specifically, this means LPCVD oxide films given either no PDA treatment or given a PDA treatment in  $\text{N}_2$  or  $\text{O}_2$  at  $700^\circ\text{C}$ . In all such films not subjected to PMA, a very rapid increase in negative  $Q_{ot}$  was observed at fluences up to  $0.00001 \text{ C-cm}^{-2}$  (i.e., less than  $10^{14}$  injected electrons/ $\text{cm}^2$ ). In all such films except those annealed in  $\text{O}_2$  at  $700^\circ\text{C}$ , this rapid initial increase in the charging curve was followed by the following sequence:

1. A decrease in net negative oxide trapped charge over the fluence range spanning  $0.0001 \text{ C-cm}^{-2}$  (less than  $10^{15}$  injected electrons/ $\text{cm}^2$ ).
2. An increase in net negative  $Q_{ot}$  during additional injection to fluences of the order of  $0.001 \text{ C-cm}^{-2}$ .

This behavior is displayed in Figure 6. The initial capture efficiencies for these films, calculated from the rapid initial rise of  $Q_{ot}$  below  $0.00001 \text{ C-cm}^{-2}$ , were approximately five percent. The effective capture efficiencies of these films during the much more gradual increase of  $Q_{ot}$  at fluences exceeding  $0.0001 \text{ C-cm}^{-2}$  were 0.001 (a tenth of a percent). These effective capture efficiencies were determined as the slope of the charging curve (e.g., Figure 6). Initial trapping efficiencies for LPCVD oxide films are tabulated in Table VI.

PMA treatment eliminated the rapid initial rise of  $Q_{ot}$  and, when present, the decrease of negative  $Q_{ot}$  over the fluence range  $0.00001$ - $0.0001 \text{ C-cm}^{-2}$ . Thus, the dominant kinetic variation observed during electron avalanche injection of LPCVD oxides given a PMA treatment was an increase of negative  $Q_{ot}$  with an initial capture efficiency of order  $(100-1000) \times 10^{-6}$ . This

behavior is manifest in the data from an LPCVD oxide given 700°C PDA and PMA treatments, displayed in Figure 7.

The data displayed in Figure 7 were similar to data observed in no-PM<sub>4</sub> oxides in the fluence range 0.0001-0.001 C-cm<sup>-2</sup> (6x10<sup>14</sup>-6x10<sup>15</sup> injected electrons/cm<sup>2</sup> in Figure 6). Within this fluence range, there is statistical evidence that the capture efficiency of films with PMA were one-half the capture efficiency of films without PMA. This conclusion is deduced from the data summarized in the Q<sub>ot</sub> column in Tables II and III. In oxides given PMA treatments, there is also statistical evidence that the initial capture efficiency of films deposited on (111) Si was less by half than that of films deposited on (100) Si. This last conclusion is drawn from the data in Table VI, or from data in the Q<sub>ot</sub> column in Tables II and III.

Finally, after electron injection to fluences exceeding 0.001 C-cm<sup>-2</sup>, it was not possible to determine the interface trap distribution D<sub>it</sub> for LPCVD oxide films not subjected to a PDA treatment at 1000°C. Large leakage currents prevented reliable low frequency C-V measurements by the quasi-static method. The single exception is listed in Table III.

### 3.2.2 LPCVD Oxides Annealed at 1000°C

Some LPCVD oxides deposited at approximately 700°C were given a PDA treatment at 1000°C. This was done because of previously reported success in producing high quality deposited oxide films via this procedure [16, 17]. Representative data from avalanche injection experiments on these oxides are displayed in Figures 5, 7, 8, and 9. The results of such measurements are tabulated in Tables II, III, and VI. These results indicate that high temperature PDA reduced the initial electron capture efficiency in LPCVD oxides by approximately two orders of magnitude (Table VI and Figure 7). PMA treatment of these films reduced initial electron capture efficiency by another two orders of magnitude (see Table VI and Figure 8).

Thus, the combined effect of a high temperature PDA treatment (annealing in N<sub>2</sub> at 1000°C) and a standard PMA treatment (annealing in H<sub>2</sub>/N<sub>2</sub> at 450°C) was a reduction of initial capture efficiency by a factor of 10<sup>-4</sup>. These results are tabulated in Table VI, specifically as a comparison between the first and the last entries for both (111) Si and (100) Si capacitors.

### 3.3 Standard and HIPOX Thermal Oxide Films

Two types of MOS dielectric films prepared by thermal oxidation of silicon were examined in this study. These were standard technological oxides produced at 1000°C in one atmosphere of dry oxygen, and HIPOX films produced at approximately 700°C in 500 atmospheres of dry oxygen. These films were prepared as absolute (standard oxide) and relative (HIPOX) standards against which the low temperature LPCVD films could be compared. The entire measurement sequence described above was executed on each type of thermal oxide. Representative data and tabulated averages for standard thermal oxides are presented in Figures 2, 4, 5, 9, and 10 and in Tables I and V. Representative data and tabulated averages for HIPOX films are presented in Figures 3, 5, 9, and 10 and in Tables II and V.

The standard thermal oxide films exhibited characteristics identical to those of standard technological oxides. In particular, the oxide charge characteristics described in Table I were similar to those summarized in E. H. Nicollian and J. R. Brews [18], and the charge trapping characteristics described in Table V were similar to those reported for dry thermal oxide films by Young and co-workers [19]. Note that in these films a PMA treatment produced an order-of-magnitude reduction in  $Q_f$ , as-grown  $D_{it}$ , post-injection  $Q_{ot}$ , and post-injection  $D_{it}$  (see Table I) and in the initial capture efficiency (see Table V).

POA treatment of HIPOX films had a relatively minor effect on oxide charge characteristics, reducing  $Q_f$ , as-grown  $D_{it}$ , and post-injection  $Q_{ot}$  by approximately one-third in films not subjected to PMA (see Table IV). PMA treatment of HIPOX films produced a two-order-of-magnitude reduction of pre-injection characteristics ( $Q_f$  and  $D_{it}$  in Table IV), but only a factor-of-two reduction of post-injection characteristics ( $Q_{ot}$  and  $D_{it}$  in Table IV).

In summary, the low temperature HIPOX films given both PDA and PMA treatments exhibited oxide charge characteristics similar to characteristics determined for standard high-temperature dry thermal oxides. In particular, the as-grown or pre-injection  $Q_f$  and  $D_{it}$  are, within overall error of the present measurement program, identical for these two types of thermal oxide film. This is appreciated by a comparison of the final entries under "As-Grown Charge" in Tables I and IV. However, values of post-injection  $Q_{ot}$  and  $D_{it}$  (Figure 5 and Tables I and IV), and the initial electron capture efficiency (Figure 9 and Table V), are approximately ten times larger in HIPOX films than in standard oxides. This point will be discussed further in Section 4.3 below.

## 4 Discussion and Conclusions

### 4.1 The Quality of LPCVD Oxide Films

The current and bias-temperature-stress measurements described in Section 3.1 indicated that deposited oxide films obtained from the dichlorosilane LPCVD process at approximately 700°C can be used to fabricate MOS capacitors with basic characteristics approaching those of capacitors fabricated on high-quality thermal oxides produced at temperatures in the vicinity of 1000°C. This required a PDA treatment in dry nitrogen or oxygen at the deposition temperature, and a standard PMA treatment. The best such films obtained in the present study, however, exhibited dark currents under electrical stress and oxide charge characteristics approximately an order-of-magnitude larger than the same quantities measured in standard high temperature thermal oxide films. These statements specifically refer to  $Q_f$  and as-grown  $D_{it}$ , i.e., to the charge characteristics of the oxide films without any electron current injection. The primary reason for the poor quality of the low temperature LPCVD oxide films was the ineffectiveness of the low temperature PDA treatments (30 minute anneals in  $N_2$  or  $O_2$  at approximately 700°C). This resulted in large densities<sup>2</sup> of interface traps  $D_{it}$ , which appeared to correlate with high dark currents under room temperature stress.

These problems were largely eliminated by high temperature PDA treatment. Thus, LPCVD films grown at 700°C and given both a PDA treatment at 1000°C and a PMA treatment exhibited as-grown dark current and oxide charge characteristics less than a factor-of-two greater than those of standard thermal oxides.

In summary, it would appear that LPCVD oxide films produced entirely at temperatures at and below 700°C will not be suitable for gate oxide applications requiring the electrical quality of standard thermal oxides. As concluded by previous investigators studying different low temperature deposition technologies, a high temperature PDA step is required to attain low interface trap densities and dark currents under stress [16].

## 4.2 Electron Injection in LPCVD Oxides

The results of the electron injection studies indicated that even the high temperature annealing treatment of low-temperature LPCVD oxide films is not sufficient to produce MOS dielectrics of the quality of standard thermal oxide films. LPCVD films annealed at 1000°C and given a PMA treatment exhibited negative  $Q_{ot}$  and post-injection  $D_{it}$  approximately one order-of-magnitude greater than those quantities measured in standard thermal oxides given the same annealing treatments. These conclusions refer to the final entries in Tables I, II, and III, and to the results displayed in Figures 5 and 9.

Thus, LPCVD oxide films produced at approximately 700°C may not be suitable for gate oxide applications requiring the full electrical quality of standard thermal oxides, even if these oxides are subjected to post-deposition annealing at 1000°C. As concluded by previous investigators studying different low temperature deposition technologies, the high temperature PDA step significantly reduced the susceptibility of LPCVD oxide films to electron trapping and to interface trap generation [17]. However, standard annealing procedures (high temperature PDA and PMA) applied to LPCVD oxides did not produce dielectric films fully equivalent to standard thermal oxides in applications requiring very low susceptibility to charge generation resulting from electron injection (short channel devices or floating gate memories).

Aside from the summary point just made, there are two facts which stood out from the electron injection measurements. First, the low temperature dichlorosilane-based LPCVD process resulted in oxide films with charge injection characteristics dominated by a very efficient electron trap. This trap was coupled to an anomalous positive charge generation, as illustrated in Figure 6. The trap, and the associated positive charge anomaly, were removed either by a high temperature PDA treatment (30 minutes in dry nitrogen at 1000°C), or by a PMA treatment. These results are manifest in the data presented in Table VI. Further analysis of this behavior is presented in Section 4.4 below.

Second, neither the PDA treatment nor the PMA treatment is the critical step in fabrication of very high quality oxide films. In such cases, the combined effect of these two annealing steps is clearly greater than the sum of the effect of each separate treatment. Thus, the LPCVD oxides given PDA at 1000°C and PMA exhibited much lower post-injection characteristics than any other type of LPCVD oxide (see Tables II and III). These observations suggest that the efficacy of the PMA treatment in H-containing atmospheres depends critically on the thermal

history of the oxide film.

#### 4.3 Properties of HIPOX Films

The PMA treatment of HIPOX films reduced the as-grown charge by more than an order-of-magnitude, and these oxides exhibited as-grown characteristics fully equivalent to those of the standard thermal oxides. However, in HIPOX films the synergistic effect of POA and PMA treatments on post-injection characteristics, described just above for LPCVD oxides, was not evident (see Table IV). Thus, the combined effect of POA and PMA in reducing  $Q_{it}$  and post-injection  $D_{it}$  is only slightly greater than sum of the independent effects of the separate treatments. In fact, the failure of the PMA treatment to greatly reduce post-injection characteristics of HIPOX films is the source of the notable difference between these films and the standard high-temperature thermal oxides.

Since all processing of the HIPOX films was at temperatures at and below  $700^{\circ}\text{C}$ , these films present a potentially significant technological advantage. Their as-grown and post-injection characteristics are superior to the best LPCVD oxides studied, and these latter films required a high temperature ( $1000^{\circ}$ ) PDA treatment. The data justifying these conclusions are presented in Tables II-VI and Figures 5 and 9.

The different post-injection trapped charge characteristics of HIPOX films and standard thermal oxides may be related to the different metallization and PMA procedures used. In particular, the HIPOX metallization was accomplished by electron beam heating of the source (versus hot filament heating for the LPCVD and standard thermal oxides). The electron beam technique is known to produce radiation damage [20]. This may result in the generation of oxide traps which survive low temperature anneals. Also, the HIPOX PMA treatment was done in dry nitrogen, versus forming gas ( $\text{H}_2/\text{N}_2$ ) for the other oxides. This could possibly alter the effect of the PMA treatment on bulk oxide and interface traps. These processing variations should be studied further.

#### 4.4 Oxide and Interface Electron Traps

As noted in Section 3.2, the oxide charging curves were, whenever possible, analyzed in terms of electron trapping centers in the bulk of the oxide film and donor-like electron traps in the vicinity of the silicon dioxide-silicon interface. The

former were presumed to capture injected electrons, and the latter to be generated by some direct or indirect mechanism involving the injected electrons. Bulk traps are characterized by a net effective areal density  $N_{ot}(\infty)$ , which is the first moment integral of the volume trap density, and by an electron capture cross section  $\sigma_c$ . The donor-like interface trap generation exponentially approaches a saturated areal density  $N_{it}(\infty)$  with a characteristic kinetic fluence interval  $1/\phi_e \cdot \sigma_e$ .  $\sigma_e$  is the effective cross section for production of interface traps by the injected electron fluence. The precise significance of this cross section, i.e., the mechanism for interface trap generation, is still a matter of considerable dispute [21].

A given charging curve was described by these kinetic parameters using Equations (1) through (4) above, with  $Q_{ot}$  negative and  $Q_{it}$  positive. The model equations giving  $Q_{ot} + Q_{it}$  as a function of  $F$  were fitted to the data (charging curves), using an iterative chi-square fitting routine. The best-fit values of the fitting parameters  $N_{ot}(\infty)$  and  $\sigma_c$ , and  $N_{it}(\infty)$  and  $\sigma_e$ , were thus determined. Partial results of these analyses are displayed in Tables VII and VIII for thermal oxides (standard and HIPOX) and for LPCVD oxides, respectively.

The most interesting result of these analyses was an electron trap with effective areal densities exceeding  $10^{13} \text{ cm}^{-2}$  and capture cross section of order  $10^{-14} \text{ cm}^2$  (see Table VIII). This trap was seen in all LPCVD oxide films not subjected to either PMA or  $1000^\circ\text{C}$  PDA treatment. It is this trap which is responsible for the anomalous electron capture in such films, for which the initial capture efficiency approaches ten percent. Results are given in Table VI, and a particular case in Figure 6.

Similar electron traps, with a capture cross section indicating a coulomb attractive trapping center, have been observed in thermal oxide films produced in water-containing oxidants at temperatures above  $1000^\circ\text{C}$  [22]. These latter traps, however, occurred with volume concentrations less than one percent of those observed in LPCVD oxides not given high temperature PDA or low temperature PMA. The average bulk concentration observed in the LPCVD oxides were of the order of  $10^{18} \text{ cm}^{-3}$ . As seen in Figure 6, these traps were associated with "anomalous positive charge" variations similar to those previously associated with generation of donor-like interface traps [11, 23]. This behavior was discussed in Section 3.2.1. Generation of interface traps has not previously been associated with coulomb attractive centers.

It is now clear that reduction of the extremely high initial electron capture efficiencies observed in as-deposited LPCVD samples by either high temperature PDA treatment or PMA treatment involved elimination of this coulomb-attractive electron trap. Detailed chemical and structural identification of this trapping

center by spectroscopic measurement could provide a detailed model for the chemical and structural changes produced by these technologically important annealing procedures.

It is also clear from the data presented in Table VIII that both steps in the sequence of high temperature PDA plus low temperature PMA in H-containing ambients eliminated specific bulk electron trapping centers in LPCVD oxides and produced a specific residual dominant center. The residual center after high temperature (10000°C) PDA was a trap with a neutral capture center cross section ( $3 \times 10^{-16} \text{ cm}^2$ ). This center was eliminated (or greatly reduced) by PMA treatment, after which the dominant trapping center had a cross section of order  $10^{-17} \text{ cm}^2$ . These results were generally similar to those previously observed in MOS dielectrics produced by thermal oxidation of silicon in steam ambients above 1000°C. In such oxides, the  $10^{-17} \text{ cm}^2$  trap was the dominant trap in films with or without PMA treatment [22].

The effect of the various anneal treatments differed in the two types of thermal oxides studied in this investigation. These results are displayed in Table VII. In the standard thermal oxide, the dominant bulk trap before PMA treatment had a cross section of  $10^{-17} \text{ cm}^2$ . After PMA treatment, the dominant trap had a cross section of order  $10^{-18} \text{ cm}^2$ . Such behavior is characteristic of nominally dry oxides, and of oxides subjected to an intentional water contamination treatment at 100-300°C [11, 24].

In summary, the LPCVD oxide films exhibited electron trapping characteristics similar to those of "wet" thermal oxides. These are different from trapping characteristics of "dry" oxides, such as the standard thermal oxide studied in this investigation. Spectroscopic studies of the several traps observed in this investigation would be useful. In particular, it would be interesting to determine whether the bulk electron trap with capture cross section approximately  $10^{-17} \text{ cm}^2$  observed in all oxide types studied in the present investigation (under some particular anneal treatment) is indeed a single specific defect.

The high-quality HIPOX films described in Tables IV and V exhibited the electron traps listed in Table VII. There is a positive charge anomaly associated with these traps, as shown by the data given in Figure 10. Neither the oxide trap nor the positive charge anomaly was strongly affected by PMA treatment. This behavior is similar to that exhibited by well-prepared high-temperature "dry" thermal oxides [11, 19, 24].

The overall quality of all silicon dioxide dielectric films appears to be quite sensitive to moisture incorporation, which is the apparent source of most serious electron trapping problems. Unintentional water contamination can occur during oxidation or deposition, during subsequent processing, or during storage of



even protected oxide films [21].

An especially interesting manifestation of this problem occurred during the studies of the HIPOX films. Bulk and interface electron trap parameters for two sets of HIPOX films studied during the present investigation are presented in Table IX. Representative data for each set are displayed in Figure 11. These films exhibited virtually identical "as-grown" film characteristics and hole trapping behavior. Nonetheless, the two sets of films had significantly different initial electron capture efficiencies (Table IX) and totally different bulk electron traps and interface trap generation kinetics (Figure 11 and Table IX). One set exhibited the dominant  $10^{-17}$  cm<sup>2</sup> electron trap characteristic of "wet" high temperature thermal oxides, the other exhibited the dominant  $10^{-18}$  cm<sup>2</sup> electron trap characteristic of "dry" high temperature thermal oxides. In each case, PMA treatment produced no significant changes in the kinetic cross sections. The probable difference between these two sets of nominally identical oxide films is unintentional water contamination during some processing step.

#### 4.5 Conclusions

The results of this research program indicated that low temperature LPCVD oxides require high temperature annealing to produce as-grown characteristics suitable for use in practical microelectronic systems. Even with high temperature annealing, the efficiency and amount of charge trapping upon avalanche electron injection may restrict their potential usefulness in VLSI or electrically alterable memory technologies.

The as-grown characteristics of low temperature HIPOX films were fully equivalent to standard thermal oxide values. The HIPOX films require no high-temperature processing step, and might be useful in developing VLSI technology. However, as in the case of the LPCVD oxides, the charge trapping developed upon avalanche injection is noticeably greater than in standard high temperature thermal oxides. The trapping behavior of HIPOX films appears to be determined by well-characterized defects. The effects of post-metallization annealing conditions on these defects should be further studied.

Finally, the present study indicated clearly that bulk oxide electron traps with four characteristic electron capture cross sections dominate the oxide charge characteristics of silicon dioxide films prepared under a variety of conditions. The depletion and enhancement of specific electron traps (as identified by capture cross section only) by specific sample

treatments (deposition or oxidation, post-fabrication annealing, and post-metallization annealing) appears to fall into two broad categories. These two categories are typified by "wet" and "dry" types of standard high temperature thermal oxides (i. e., those produced in water containing oxidants and those produced in reasonably dry oxygen). This comprehensive hypothesis is based on incomplete experimental information, since the capture cross section is a relatively non-discriminatory parameter for trap classification. It would be very helpful to refine the trap classification with spectroscopic studies yielding trap depths or other optical or thermal characteristics [22].

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TABLE I. OXIDE CHARGE IN (111) DRY THERMAL OXIDE, 58 nm THICK

OXIDATION CONDITIONS: 1 atm dry O<sub>2</sub>, 1000°C, 40 min

Annealing		As-Grown Charge		Post-Injection Characteristics		
POA		Q <sub>f</sub>	D <sub>it</sub>	F <sub>A</sub>	Q <sub>ot</sub>	D <sub>it</sub>
(N <sub>2</sub> ambient						
T = 1000°C		(10 <sup>11</sup>	(10 <sup>11</sup>		(10 <sup>11</sup>	(10 <sup>11</sup>
t = 30 min)		cm <sup>-2</sup> )	cm <sup>-2</sup> -eV <sup>-1</sup> )	(C-cm <sup>-2</sup> )	cm <sup>-2</sup> )	cm <sup>-2</sup> -eV <sup>-1</sup> )
PMA						
POA	no PMA	5	2	0.05	12	40
POA	PMA	1	0.1-0.4	0.05	1-2	4

TABLE II. OXIDE CHARGE IN (111) DEPOSITED OXIDE, ~33 nm THICK  
 DEPOSITION CONDITIONS: 1 torr  $\text{SiH}_2\text{Cl}_2:\text{N}_2\text{O}$  (1:10), ~700°C, 120 min

Annealing	As-Grown Charge		Post-Injection Characteristics		
PDA (ambient and T as listed t = 30 min)	$Q_f$ ( $10^{11}$ $\text{cm}^{-2}$ )	$D_{it}$ ( $10^{11}$ $\text{cm}^{-2}\text{-eV}^{-1}$ )	$F_A$ ( $\text{C}\text{-cm}^{-2}$ )	$Q_{ot}$ ( $10^{11}$ $\text{cm}^{-2}$ )	$D_{it}$ ( $10^{11}$ $\text{cm}^{-2}\text{-eV}^{-1}$ )
PMA					
no PDA no PMA	8	20	0.001	80	--
no PDA PMA	4	1	0.001	40	--
PDA 700°C $\text{O}_2$ no PMA	17	>100(?)	0.001	150	--
PDA 700°C $\text{O}_2$ PMA	4	2	0.001	13	--
PDA 700°C $\text{N}_2$ no PMA	10	20	0.001	30	--
PDA 700°C $\text{N}_2$ PMA	3	2	0.001	15	--
PDA 800°C $\text{N}_2$ PMA	3	1	0.001	10	--
PDA 1000°C $\text{N}_2$ no PMA	8	1	0.001	50	--
PDA 1000°C $\text{N}_2$ PMA	3	0.1-0.6	0.001 0.05	<1 22	-- 20

TABLE III. OXIDE CHARGE IN (100) DEPOSITED OXIDE, ~40 nm THICK  
DEPOSITION CONDITIONS: 1 torr SiH<sub>2</sub>Cl<sub>2</sub>:N<sub>2</sub>O (1:10), ~720°C, 120 min

Annealing	As-Grown Charge		Post-Injection Characteristics		
PDA	Q <sub>f</sub>	D <sub>it</sub>	F <sub>A</sub>	Q <sub>ot</sub>	D <sub>it</sub>
(N <sub>2</sub> ambient T as listed t = 30 min)	(10 <sup>11</sup> cm <sup>-2</sup> )	(10 <sup>11</sup> cm <sup>-2</sup> -eV <sup>-1</sup> )	(C-cm <sup>-2</sup> )	(10 <sup>11</sup> cm <sup>-2</sup> )	(10 <sup>11</sup> cm <sup>-2</sup> -eV <sup>-1</sup> )
PMA					
no PDA no PMA	6	15	0.001	50	--
no PDA PMA	1	4	0.001	65	--
PDA 720°C N <sub>2</sub> no PMA	8	4	0.0001	90	--
PDA 720°C N <sub>2</sub> PMA	2	3	0.001	36	12
PDA 1000°C N <sub>2</sub> no PMA	4	1	0.001	26	--
PDA 1000°C N <sub>2</sub> PMA	7	1	0.001 0.05	2 8	-- 48

TABLE IV. OXIDE CHARGE IN (100) DRY THERMAL OXIDE, 40 & 90 nm THICK  
 OXIDATION CONDITIONS: 500 atm dry O<sub>2</sub>, 685°C, 60 and 165 min\*

Annealing		As-Grown Charge		Post-Injection Characteristics		
POA		Q <sub>f</sub>	D <sub>it</sub>	F <sub>A</sub>	Q <sub>ot</sub>	D <sub>it</sub>
(N <sub>2</sub> ambient T = 685°C t = 300 min)		(10 <sup>11</sup> cm <sup>-2</sup> )	(10 <sup>11</sup> cm <sup>-2</sup> -eV <sup>-1</sup> )	(C-cm <sup>-2</sup> )	(10 <sup>11</sup> cm <sup>-2</sup> )	(10 <sup>11</sup> cm <sup>-2</sup> -eV <sup>-1</sup> )
PMA						
no POA	no PMA	31	80	0.05	47	--
no POA	PMA	3	1	0.05	23	60
POA	no PMA	21	60	0.05	33	75
POA	PMA	<1	0.2-0.7	0.05	15	28

\* The results quoted above are averaged from data obtained on samples of two different thicknesses. There was no evidence of any oxide charge dependence on oxide thickness.



TABLE V. THERMAL OXIDE INITIAL ELECTRON CAPTURE EFFICIENCY

Thermal Oxidation Conditions Annealing Conditions	Initial Electron Capture Efficiency
(111) Si, 1 atm O <sub>2</sub> , 1000°C	
1000°C N <sub>2</sub> POA and no PMA	10x10 <sup>-6</sup>
1000°C N <sub>2</sub> POA plus PMA	0.4x10 <sup>-6</sup>
(100) Si, 500 atm O <sub>2</sub> , 685°C	
no POA but with PMA	10x10 <sup>-6</sup>
685°C N <sub>2</sub> POA plus PMA	10x10 <sup>-6</sup>

TABLE VI. LPCVD OXIDE INITIAL ELECTRON CAPTURE EFFICIENCY

SiH <sub>2</sub> Cl <sub>2</sub> :N <sub>2</sub> O Deposition Conditions Annealing Conditions	Initial Electron Capture Efficiency
(111) Si, 1 torr, 700°C	
no PDA and no PMA	50,000x10 <sup>-6</sup>
no PDA but with PMA	800x10 <sup>-6</sup>
700°C O <sub>2</sub> PDA and no PMA	50,000x10 <sup>-6</sup>
700°C O <sub>2</sub> PDA plus PMA	200x10 <sup>-6</sup>
700°C N <sub>2</sub> PDA and no PMA	70,000x10 <sup>-6</sup>
700°C N <sub>2</sub> PDA plus PMA	300x10 <sup>-6</sup>
800°C N <sub>2</sub> PDA plus PMA	200x10 <sup>-6</sup>
1000°C N <sub>2</sub> PDA and no PMA	700x10 <sup>-6</sup>
1000°C N <sub>2</sub> PDA plus PMA	6x10 <sup>-6</sup>
(100) Si, 1 torr, 720°C	
no PDA and no PMA	40,000x10 <sup>-6</sup> (?)
no PDA but with PMA	2000x10 <sup>-6</sup>
720°C N <sub>2</sub> PDA and no PMA	70,000x10 <sup>-6</sup>
720°C N <sub>2</sub> PDA plus PMA	1000x10 <sup>-6</sup>
1000°C N <sub>2</sub> PDA and no PMA	800x10 <sup>-6</sup>
1000°C N <sub>2</sub> PDA plus PMA	8x10 <sup>-6</sup>

TABLE VII. DOMINANT ELECTRON TRAPS IN THERMAL OXIDES

Oxidation Annealing	Electron Capture Cross Section ( $\text{cm}^2$ )	Areal Density of Dominant Trap ( $\text{cm}^{-2}$ )
(111) Si, 1 atm $\text{O}_2$ , $1000^\circ\text{C}$		
1000°C $\text{N}_2$ POA, no PMA	$1 \times 10^{-17}$	$1 \times 10^{12}$
1000°C $\text{N}_2$ POA plus PMA	$1 \times 10^{-18}$	$5 \times 10^{11}$
(100) Si, 500 atm $\text{O}_2$ , $685^\circ\text{C}$		
no POA but with PMA	$4 \times 10^{-18}$	$3 \times 10^{12}$
$685^\circ\text{C}$ $\text{N}_2$ POA plus PMA	$3 \times 10^{-18}$	$3 \times 10^{12}$

TABLE VIII. DOMINANT ELECTRON TRAPS IN DEPOSITED OXIDES

SiH <sub>2</sub> Cl <sub>2</sub> :N <sub>2</sub> O Deposition Annealing	Electron Capture Cross Section (cm <sup>2</sup> )	Areal Density of Dominant Trap (cm <sup>-2</sup> )
(111) Si, 1 torr, 720°C		
720°C O <sub>2</sub> PDA, no PMA	5x10 <sup>-15</sup>	>1x10 <sup>13</sup>
(100) Si, 1 torr, 720°C		
1000°C N <sub>2</sub> PDA, no PMA	3x10 <sup>-16</sup>	3x10 <sup>12</sup>
1000°C N <sub>2</sub> PDA plus PMA	1x10 <sup>-17</sup>	1x10 <sup>12</sup>

TABLE IX. BULK AND INTERFACE ELECTRON TRAPS IN HIPOX FILMS

OXIDATION CONDITIONS: 500 atm dry O<sub>2</sub>, 685°C, 60 and 165 min

Annealing		Bulk Electron Trapping			Interface Traps	
		$\sigma_c$	$N(\infty)$	Initial Electron Capture Efficiency	$\sigma_e$	$N(\infty)$
POA (N <sub>2</sub> ambient T = 685°C t = 300 min)		(10 <sup>-18</sup> cm <sup>2</sup> )	(10 <sup>11</sup> cm <sup>-2</sup> )		(10 <sup>-18</sup> cm <sup>2</sup> )	(10 <sup>11</sup> cm <sup>-2</sup> )
PMA						
"WET" OXIDE, 40 nm thick						
no POA	no PMA	20	40	50X10 <sup>-6</sup>	1	20
no POA	PMA	10	40	40X10 <sup>-6</sup>	1	30
POA	no PMA	20	20	50X10 <sup>-6</sup>	2	20
POA	PMA	10	20	25X10 <sup>-6</sup>	1	20
"DRY" OXIDE, 90 nm thick						
no POA	PMA	4	30	13X10 <sup>-6</sup>	0.4	10
POA	PMA	3	30	9X10 <sup>-6</sup>	0.2	9

## Figure Captions

Figure 1. Normalized high frequency and quasi-static low frequency capacitance characteristics  $C/C_{ox}$  for an MOS device fabricated on an LPCVD oxide film. The device was given a  $1000^{\circ}\text{C}$  PDA treatment and a PMA treatment. Solid points are data obtained on the as-fabricated device; open points are data obtained after avalanche electron injection to a fluence of  $0.05 \text{ C-cm}^{-2}$ . The heavy solid lines are the capacitance characteristics of an ideal device.

Figure 2. Normalized high frequency and quasi-static low frequency capacitance characteristics  $C/C_{ox}$  for an MOS device fabricated on a standard high temperature dry thermal oxide film. The device was given a  $1000^{\circ}\text{C}$  POA treatment and a PMA treatment. Solid points are data obtained on the as-fabricated device; open points are data obtained after avalanche electron injection to a fluence of  $0.05 \text{ C-cm}^{-2}$ .

Figure 3. Normalized high frequency and quasi-static low frequency capacitance characteristics  $C/C_{ox}$  for an MOS device fabricated on a HIPOX low temperature dry thermal oxide film. The device was given a  $685^{\circ}\text{C}$  POA treatment and a PMA treatment. Solid points are data obtained on the as-fabricated device; open points are data obtained after avalanche electron injection to a fluence of  $0.05 \text{ C-cm}^{-2}$ .

Figure 4. Interface trap distributions determined from analysis of high frequency and low frequency C-V characteristics. These results were all obtained on as-fabricated devices not subjected to avalanche electron injection. The devices were fabricated on different types of oxide films, as indicated. All samples were given a PMA treatment.

Figure 5. Interface trap distributions determined from analysis of high frequency and low frequency C-V characteristics. These results were all obtained on devices subjected to avalanche electron injection to a fluence of  $0.05 \text{ C-cm}^{-2}$ . All samples were given both POA/PDA and PMA treatments, as described in the captions to Figures 1-3. The solid data points at the bottom of the figure were obtained from a capacitor incorporating an as-fabricated standard thermal oxide film, and are also shown in Figure 4.

Figure 6. Oxide charging curve determined from C-V tracking data obtained during avalanche electron injection. These data were

obtained on a device fabricated on an LPCVD oxide film given a 700°C PDA treatment. The device was not given a PMA treatment.

Figure 7. Oxide charging curves determined from C-V tracking data obtained during avalanche electron injection. These data were obtained on devices fabricated on LPCVD oxide films given either a 700°C PDA treatment or a 1000°C PDA treatment, as indicated. Both devices were given a PMA treatment.

Figure 8. Oxide charging curves determined from C-V tracking data obtained during avalanche electron injection. These data were obtained on devices fabricated on LPCVD oxide films given a 1000°C PDA treatment. Results are shown for devices with and without a PMA treatment, as indicated.

Figure 9. Oxide charging curves determined from C-V tracking data obtained during avalanche electron injection. Results are shown for devices fabricated on three different types of oxide film, as indicated. The HIPOX and standard thermal oxide samples were given both POA and PMA treatments. The LPCVD oxide samples were given both 1000°C PDA and PMA treatments.

Figure 10. Oxide charging curves determined from C-V tracking data obtained during avalanche electron injection. Results shown were obtained during large fluence injections on the best devices examined during the present study. These devices were fabricated on HIPOX low temperature thermal oxides and standard high temperature thermal oxides, as indicated. All samples were given both POA and PMA treatments.

Figure 11. Oxide charging curves determined from C-V tracking data obtained during avalanche electron injection. These data were obtained from devices fabricated on HIPOX low temperature thermal oxide films given a 685°C PDA treatment and a PMA treatment. The fabrication technology was nominally identical for these two films. The observed charging behavior is that characteristic of "dry" or "wet" standard high-temperature thermal oxide films, as indicated.

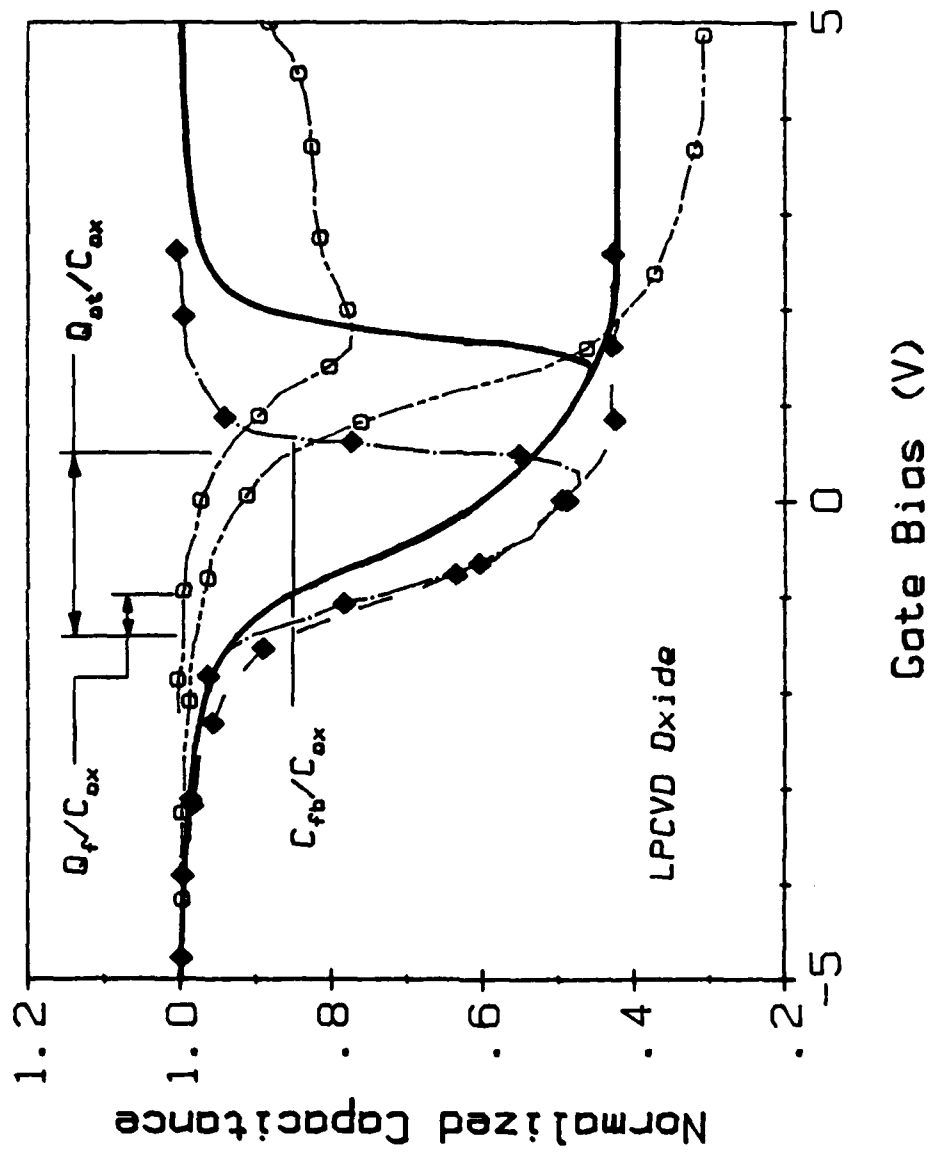


Fig. 1



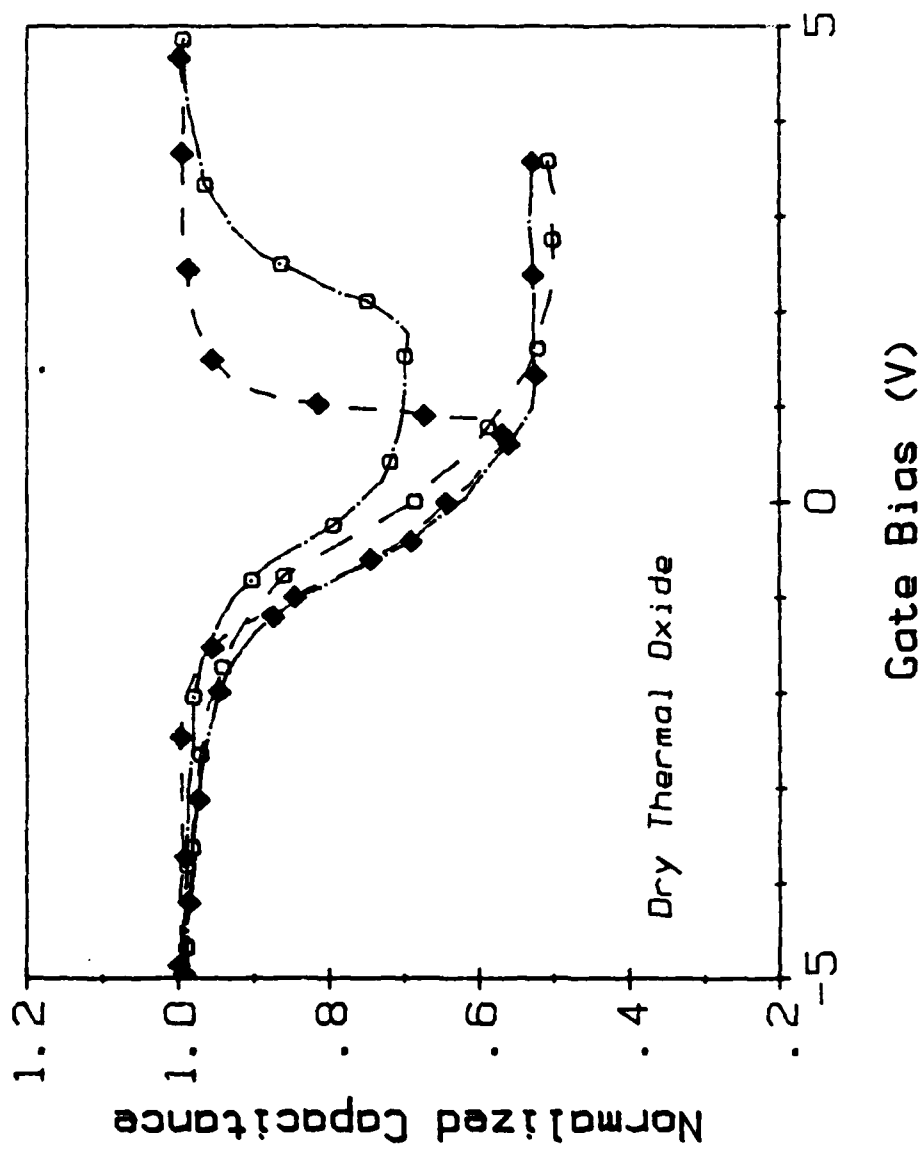


Fig. 2

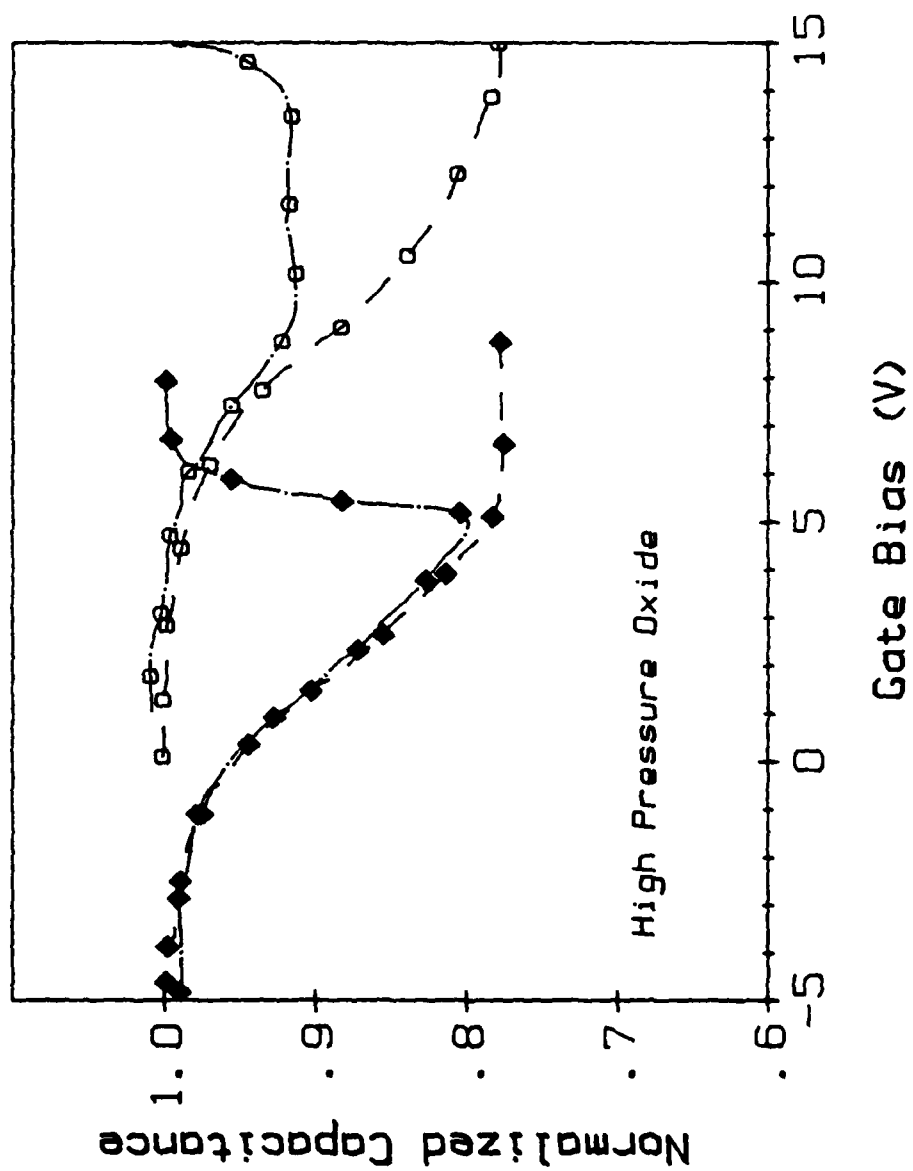


Fig. 3

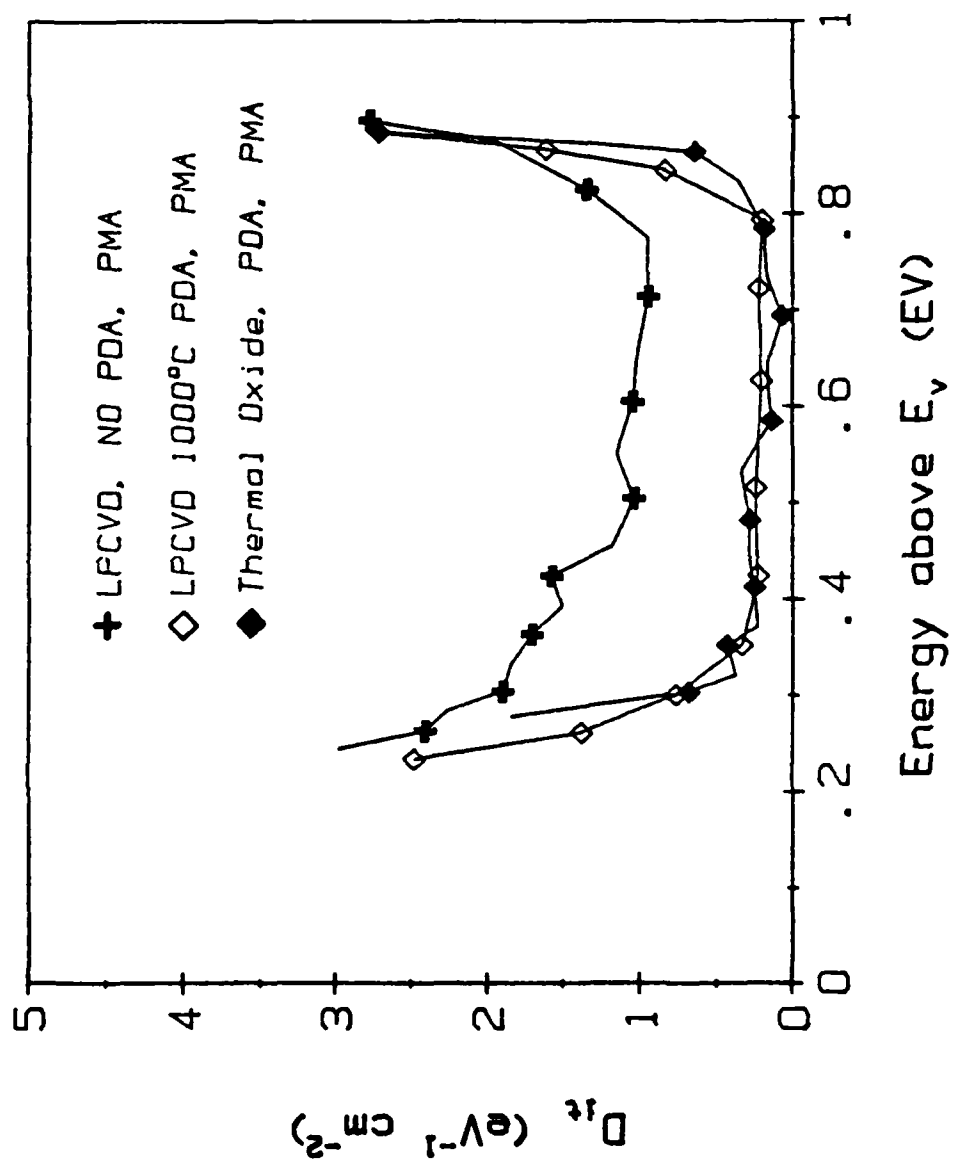


Fig. 4

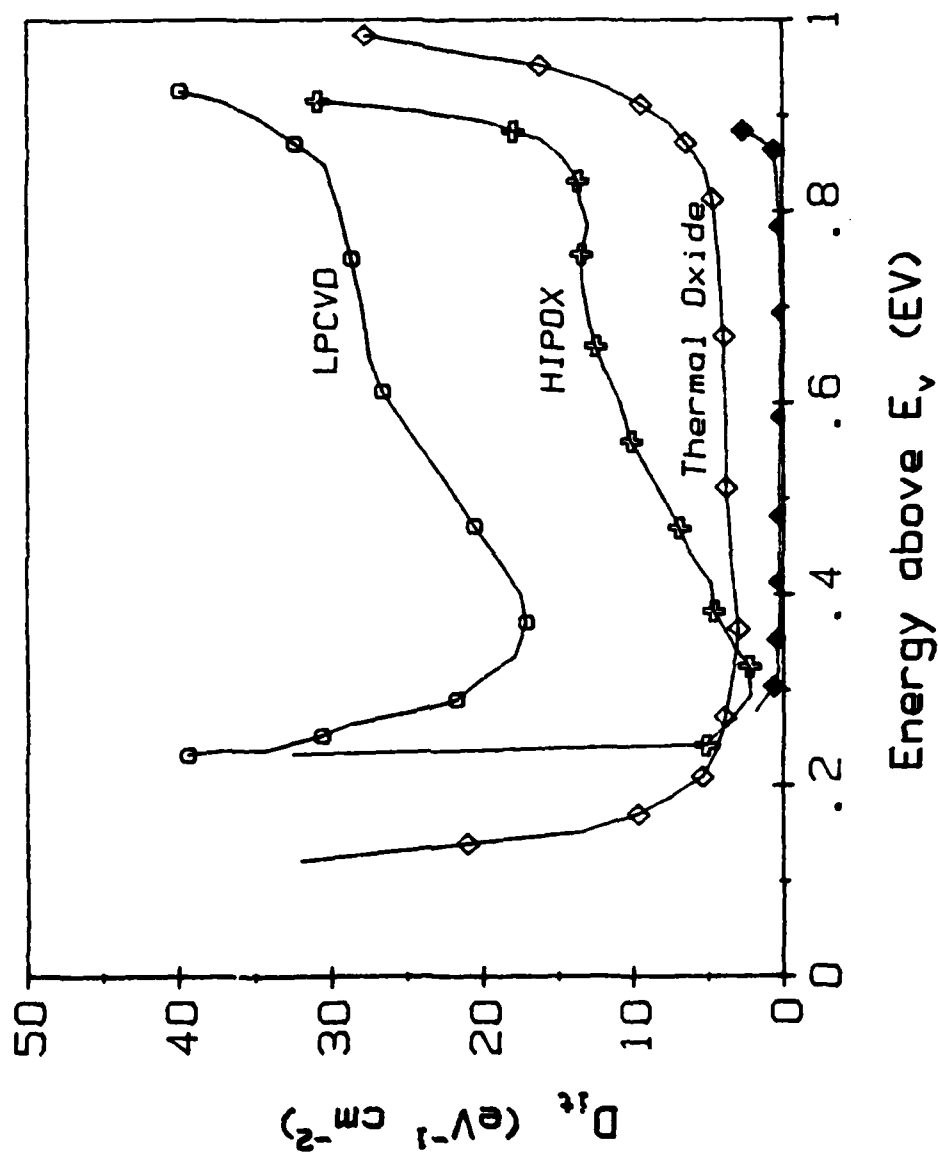


Fig. 5

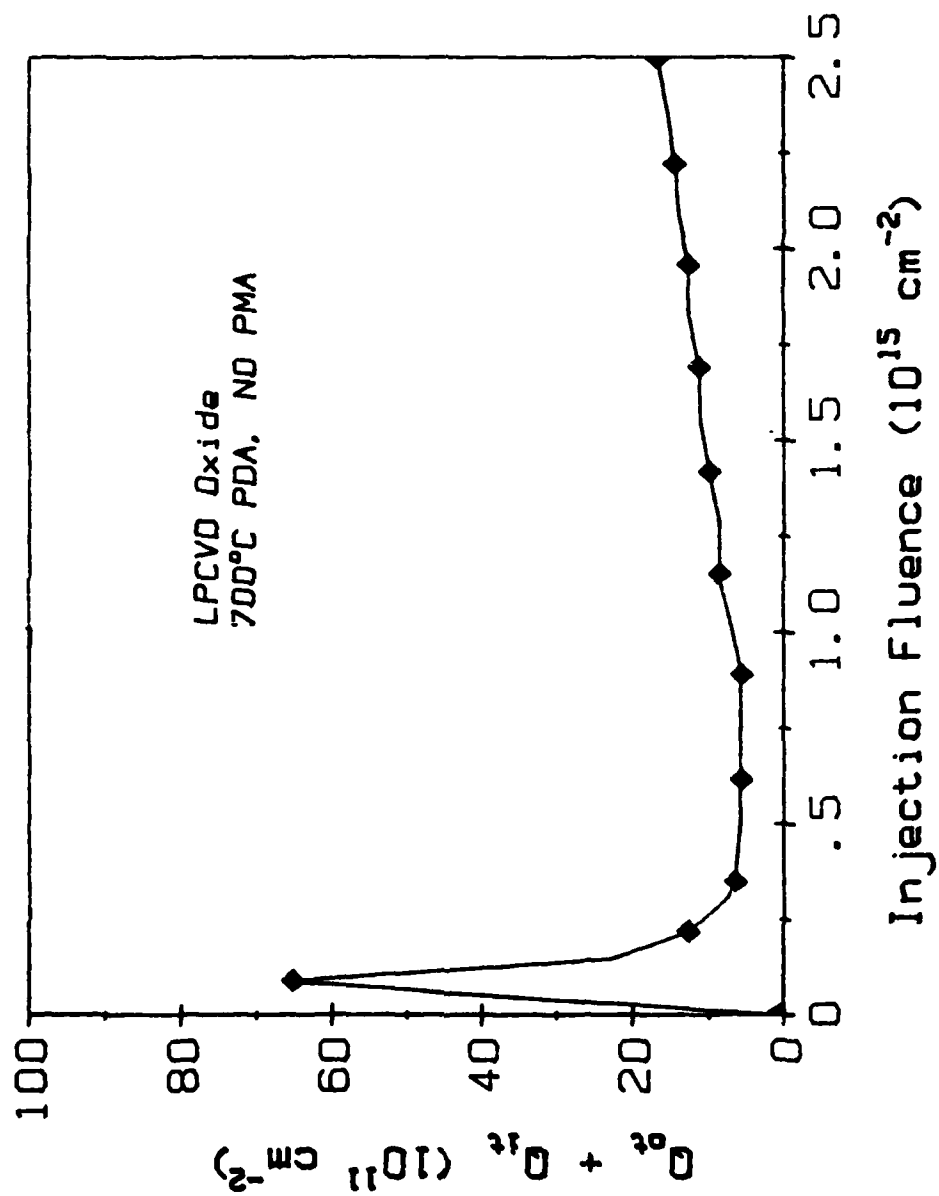


Fig. 6

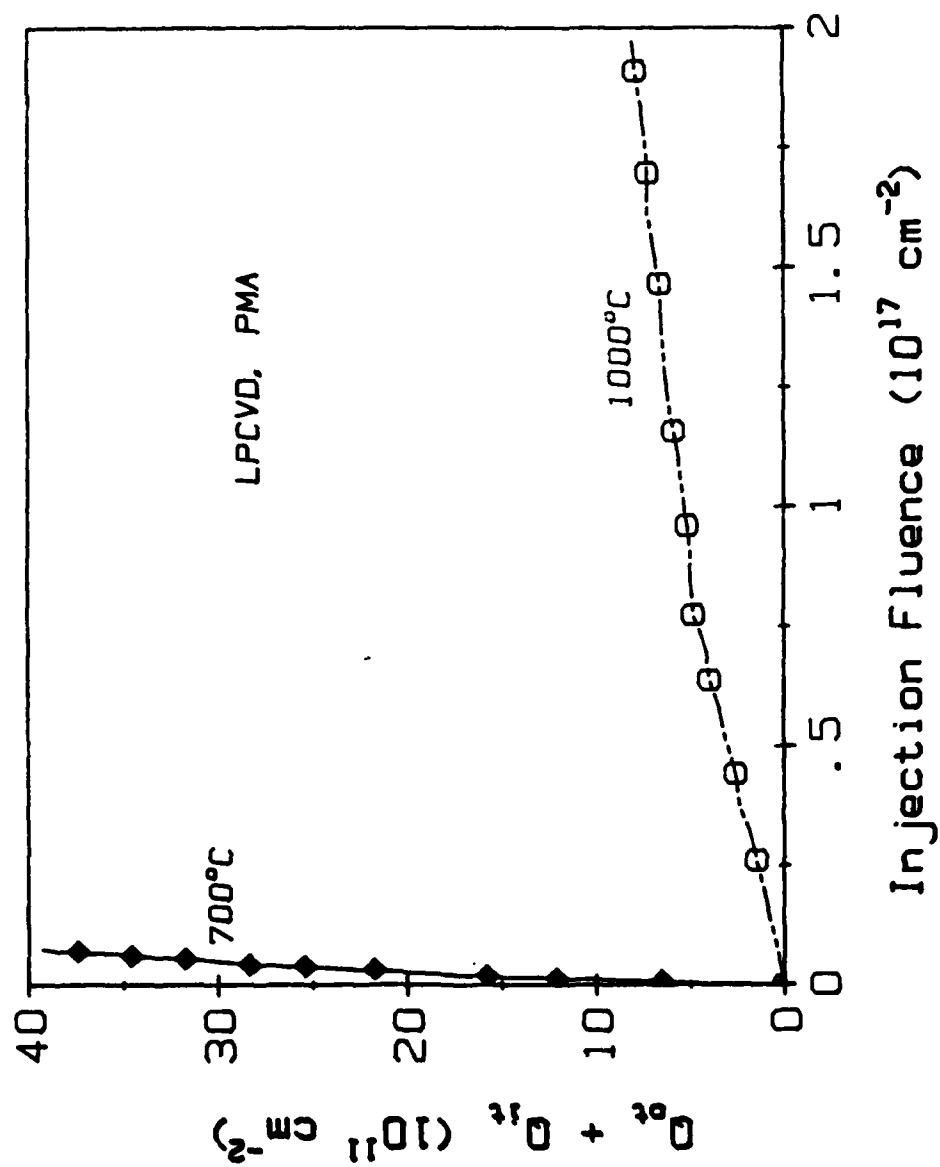


Fig. 7

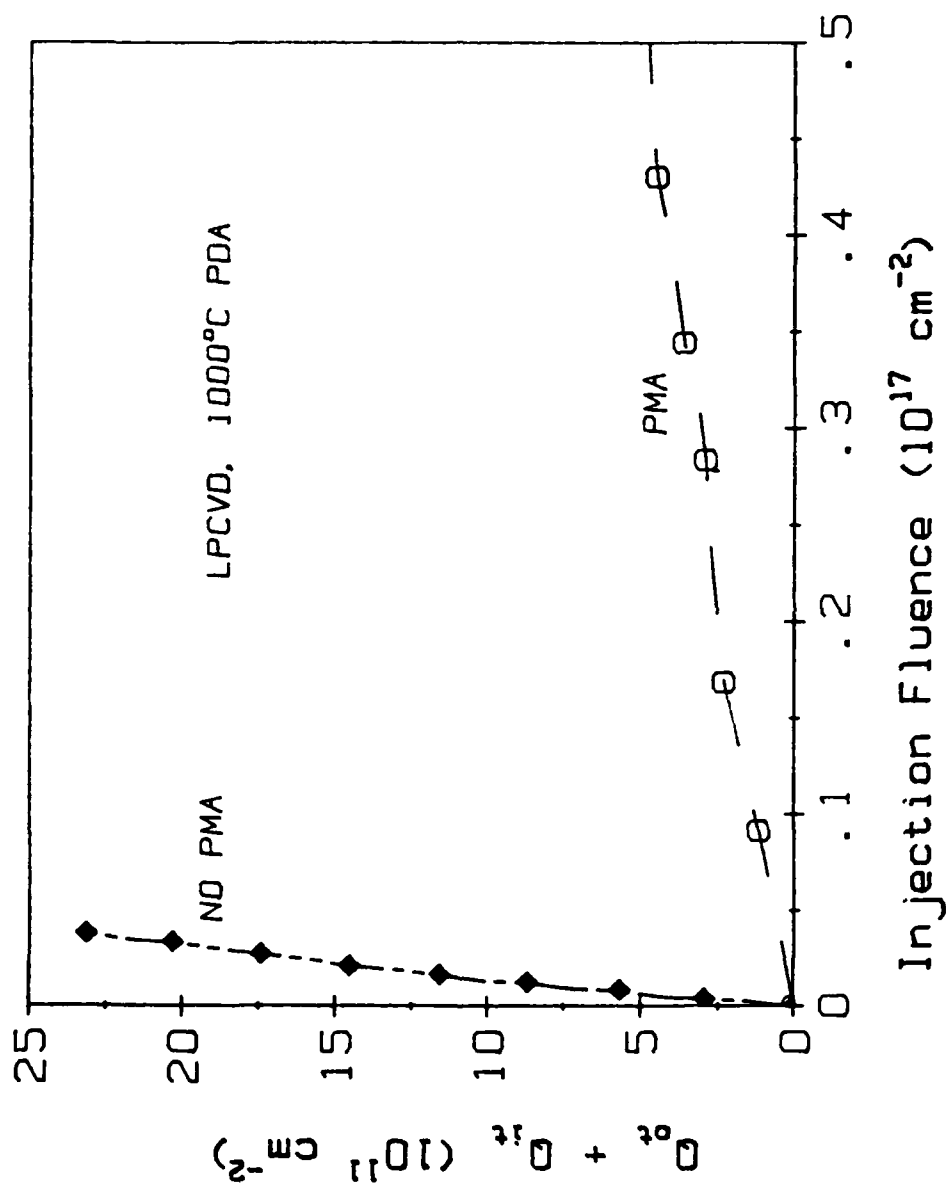


Fig. 8

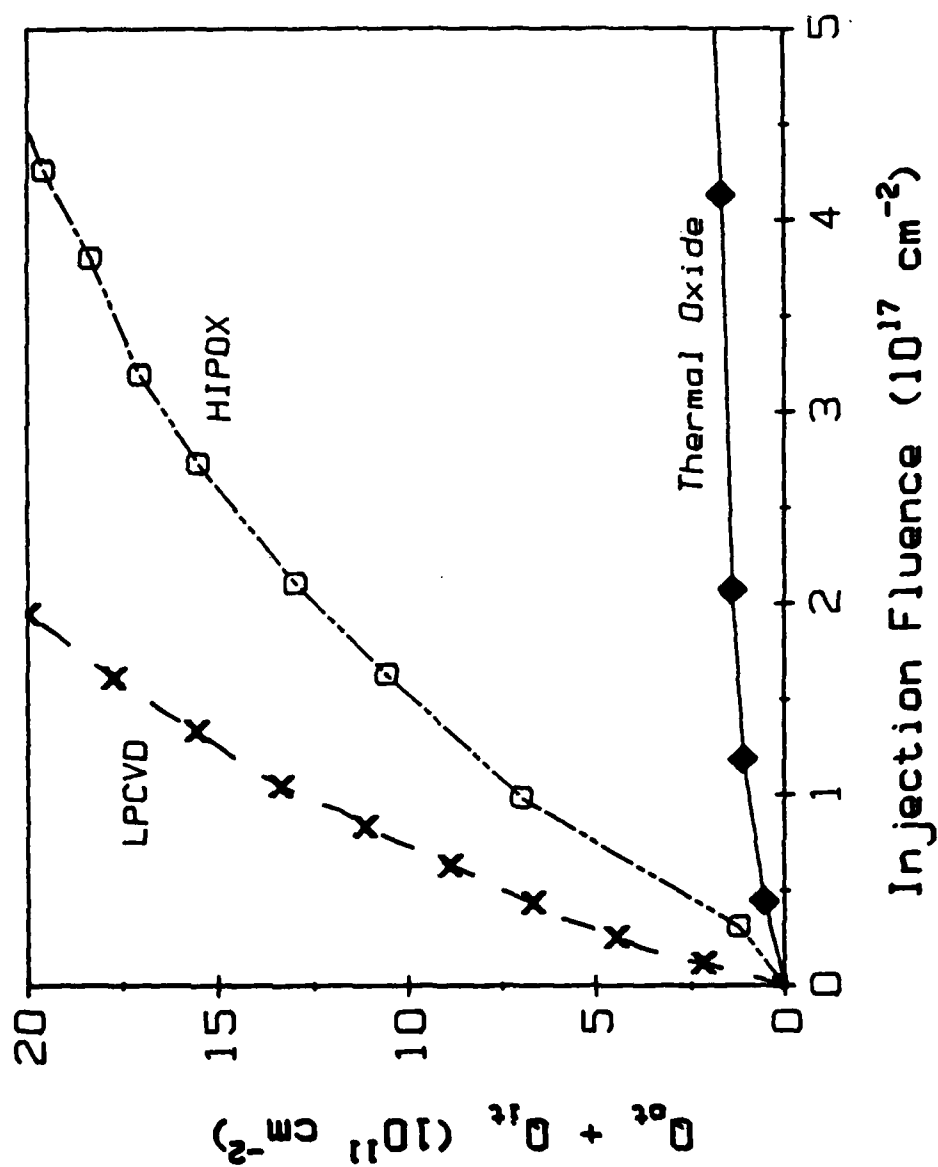


Fig. 9  
Pg. 43



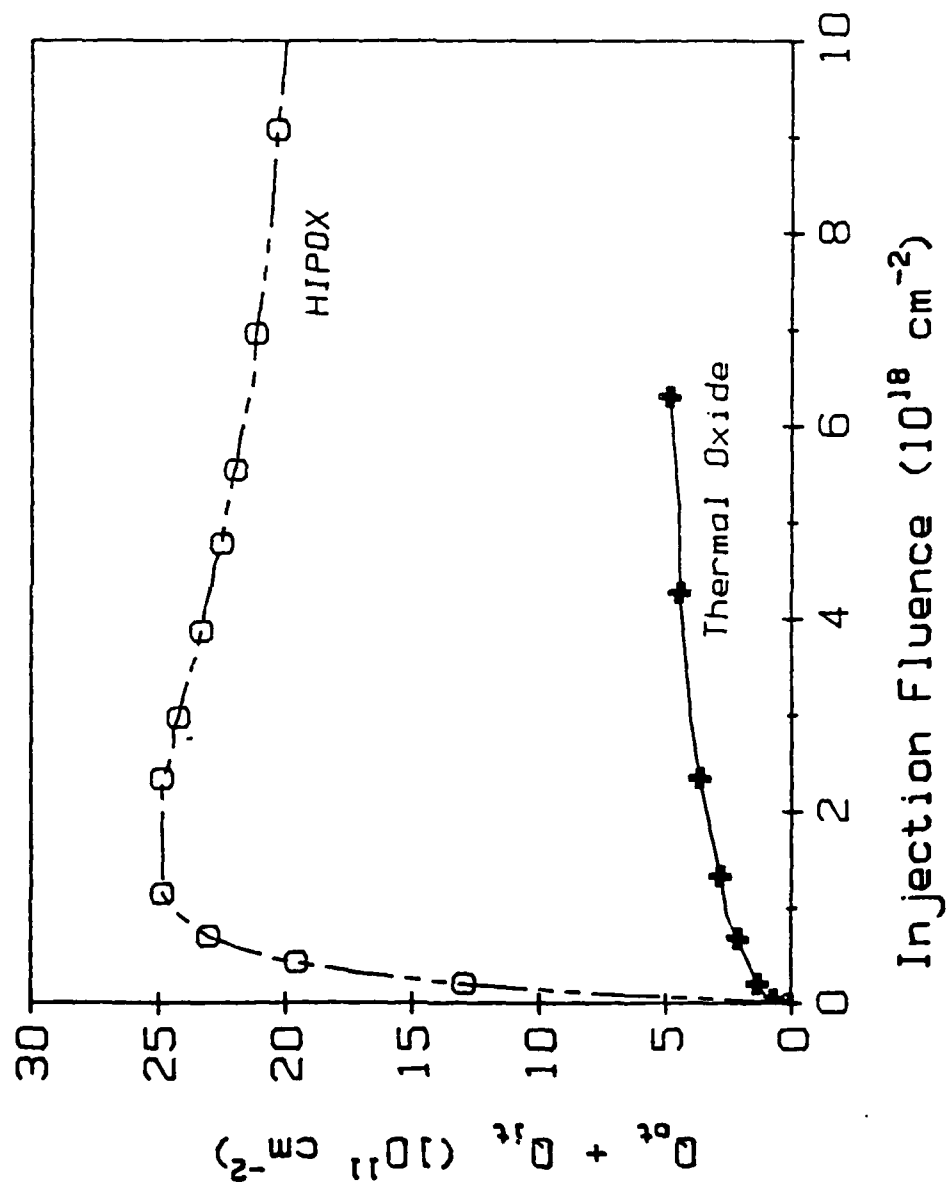


Fig. 10  
Pg. 44

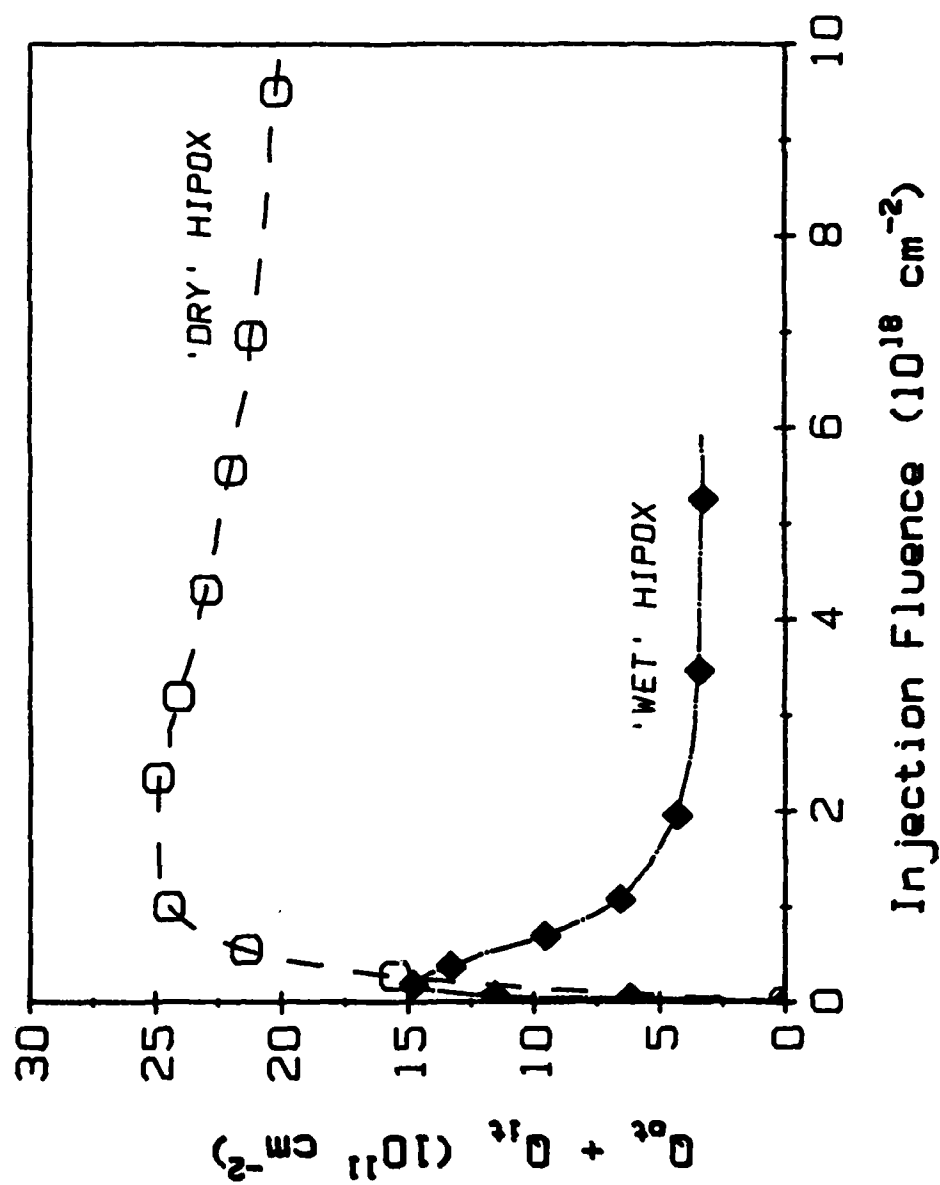


Fig. 11  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  Metal-oxide-silicon (MOS) capacitors were fabricated on silicon dioxide films produced at 700°C by either low pressure chemical vapor deposition (LPCVD) or high pressure thermal oxidation (HIPOX). The LPCVD process involved reaction of dichlorosilane with nitrous oxide. The HIPOX process involved dry oxygen. The LPCVD and HIPOX films were subjected to a variety of annealing treatments. We have systematically investigated the effects of these treatments by measurement of oxide charge and interface trap density before and after electron current transport across the oxide film. The as-grown electrical characteristics of		

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20. Abstract Continued

HIPOX films, grown and annealed at 700°C, were comparable to those of standard dry thermal oxides grown and annealed at 1000°C. However, charge trapping in the HIPOX films was an order of magnitude larger than in the standard oxides, although well-prepared HIPOX films exhibited specific electron traps characteristic of standard dry oxides. The LPCVD oxide films required a 1000°C anneal to produce as-grown and trapped charge characteristics comparable to those of the HIPOX films. In the LPCVD oxides, a series of electron traps with cross sections ranging from  $10^{-17}$  to  $10^{-14}$  cm<sup>2</sup> were systematically altered by annealing treatments. In general, the electron traps in LPCVD oxide films produced by the nitrous oxide-dichlorosilane process were similar to those in standard wet oxides, produced by thermal oxidation in water vapor above 1000°C.

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